Nitrogen-doped graphene/carbon nanotube self-assembly for efficient oxygen reduction reaction in acid media

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ARTICLE INFO

ABSTRACT

Graphene, a two-dimensional layer structure of sp^2-hybridized carbon, has garnered a great deal of attention as a promising material in electrochemistry. However, graphene has strong direction-dependent transport properties and is easily restacked to graphite; further development of graphene technology should thus be pursued for applications related to electrochemistry. Herein, a graphene/CNT self-assembly (GCA) was synthesized through the electrostatic interaction between graphene and CNTs, and was applied as a catalyst for oxygen reduction reactions (ORRs) in acid media after modification with N-doping. We demonstrated that the assembly with CNTs effectively increases the electric conductivity and hinders restacking of graphene layers, inducing facile transfer of electrons through CNTs and of reactants (e.g. oxygen and protons) through the interspace of graphene layers. The construction of highways for electrons and reactants on graphene layers resulted in 0.91 V onset potential and 2.13 mA/mg ORR activity at 0.75 V in acid media, representing significantly improved performance compared with that of catalysts derived from only graphene (0.86 V, 0.34 mA/mg) or CNTs (0.80 V, 0.02 mA/mg). In addition, the N-modified GCA shows much higher durability than that of only graphene, CNT or commercial Pt/C catalysts in severe operation conditions, with low production of peroxide in ORRs.

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1. Introduction

Nitrogen-doped carbon materials with and without trace amounts of transition metals have been highlighted as non-precious metal catalysts for oxygen reduction reactions (ORRs) due to their high methanol/CO tolerance, good stability, and low price [1–11]. In alkaline media, various carbon materials reveal outstanding ORR performances which are comparable to that of a Pt catalyst [6–13]. However, the carbon materials unfortunately demonstrate much lower ORR activity compared to a Pt catalyst in acid media [1–5], which is the actual environment of polymer electrolyte membrane fuel cells (PEMFCs).

Since its discovery, graphene has enabled significant advancement of energy conversion and storage technologies due to its superior electrical and mechanical properties originating from the two-dimensional layered structure of sp^2-hybridized carbon [14,15]. However, as a non-noble metal catalyst for ORRs in acid media, graphene-derived materials reveal no outstanding catalytic activity compared with those of other carbon-derived catalysts

[16–20]. Recently, through experimental and theoretical studies, Banks and coworkers proposed that graphene may not be a beneficial electrode material, as the large basal plane of graphene impedes efficient electron transfer and results in slow kinetics in electrochemical reactions [21]. Moreover, graphene layers are easily agglomerated and restacked by van der Waals interactions [22]. With respect to catalysis, restacking of graphene impedes facile transport of reactants between the graphene layers and reduces the number of active sites participating in the reaction, resulting in declined catalytic activity.

To secure high applicability of graphene as an electrode material, a graphene/CNT self-assembly (GCA) was developed and examined as a catalyst for ORRs in acid media after N-modification. Recently, Zhang et al. synthesized Fe-N doped CNT/graphene composite through growth of CNT on graphene layers, and reveals good ORR performance of the composite resulted from the uniform nucleation and growth of N-doped CNTs [23]. Contrary to the previous report, our strategy for graphene/CNT self-assembly centered on the deposition of CNTs on the graphene layers; thus, in the assembly, CNTs act as circuits for facile electron transfer and as spacers for preventing restacking of graphene layers, introducing interlayer spaces for effective transport of the reactants (Scheme 1). Similar methods have been explored in the area of
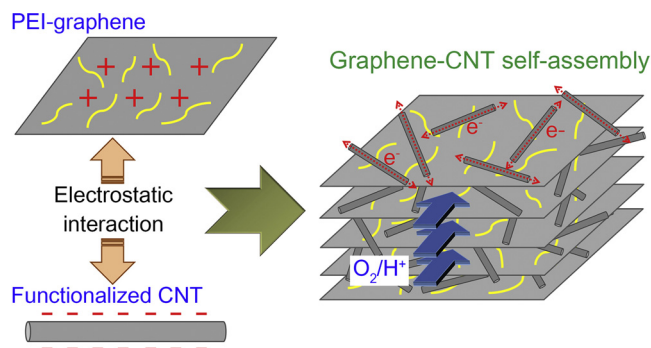
Scheme 1. Strategy for enhancing the applicability of graphene as an electrode material.

super-capacitors [24–27], but we examined this strategy for application of graphene as an electro-catalytic material toward ORRs in acid media. Self-assembly was performed by electrostatic interaction between poly-ethyleneimine (PEI)-modified graphene having a positive charge and acid-treated CNT having a negative charge [28]. The PEI-modified graphene was synthesized from graphite oxide (GO, Fig. S1). For application as ORR catalysts, N was doped into the prepared carbon materials through pyrolysis with dicyandiamide and small amounts of transition metal chlorides (Co and Fe), followed by acid-treatment to eliminate the metals [19,29]. Finally, three-different catalysts were obtained: N-doped CNTs (NCNT), N-doped graphene (NGr), and N-doped GCA (NGCA).

2. Experimental

2.1. Preparation of GO, graphene, and GCA, and N-modifications

All chemicals were obtained from Aldrich. The GO was prepared by using methods reported elsewhere [30]. Briefly, graphite (3 g) was dispersed in a concentrated acid mixture of H_2SO_4 and H_3PO_4. After the addition of $KMnO_4$ (18 g), the solution was heated at 50 °C for 12 h. The solution was poured onto ice (400 mL), and then H_2O_2 (5 mL) was added. The GO was obtained after an iterative centrifuge with a HCl solution and deionized (DI) water. The graphene was synthesized by reduction of GO (0.2 g) with hydrazine (0.6 mL) as reducing agent at 95 °C.

Self-assembly of graphene and CNTs was performed by electrostatic interaction between surface modified graphene and CNTs [28]. The graphene surface was modified with poly(ethyleneimine). The GO (0.2 g) was dispersed by ultra-sonication in DI-water (200 mL). After the addition of PEI solution (50 wt.%, 6 g), the GO solution was stirred at 60 °C for 12 h. After cooling the solution to room temperature, GO was reduced by the same procedure as employed for graphene. The surface of CNTs (0.5 g) was acid-treated with concentrated H_2SO_4 (150 mL) and HNO_3 (50 mL) at 70 °C for 90 min. For self-assembly, surface modified graphene and CNTs (graphene: CNTs = 3:1 wt. ratio) were well-dispersed in 200 mL of DI-water by ultra-sonication for 1 h, and then self-assembly proceeded under stirring for 1 h. The GCA was finally obtained by centrifugation, washing with DI-water, and drying in a vacuum oven.

During the synthesis procedures, hydrazine was used as reducing agent but it was also able to act as N-doping source in the reaction. However, the effect of hydrazine on the ORR activity of carbon material is not significant and further N-modification step should be followed [31]. N-modification of the CNTs, graphene, and GCA was performed by pyrolysis of a mixture of carbon-material (0.2 g), $CoCl_2 \cdot 6H_2O$ (2 mg), $FeCl_2 \cdot 4H_2O$ (5 mg), and DCDA (0.4 g). It is well known that the presence of trace amount of metal in pyrolysis step assist generation of highly active

carbon-derived catalysts for ORRs in acid media [32]. All precursors were dissolved in DI-water (50 mL), and sonicated for 1 h. A solid mixture was obtained after evaporation of the solution, and the powder was heat-treated at 900 °C for 3 h under an Ar atmosphere. Acid leaching was conducted in a H_2SO_4 solution (0.5 M, 100 mL) for 8 h at 80 °C to dissolve acid-unstable metal phases. Finally, this procedure was conducted once again.

2.2. Physical characterizations

The physical properties of the graphene-derived catalysts were examined via four-point probe, X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), element analysis (EA), and inductively coupled plasma (ICP).

The sheet resistivity of carbon film was obtained by a CMT-SR2000NW (Advanced Instrument Technology). The carbon film was prepared on a slide glass substrate by spraying carbon-polytetrafluoroethylene (PTFE) ink (Carbon: PTFE = 3 wt.:1 wt.). The XRD patterns were acquired from a D/MAX-2500 (Rigaku) operated at 40 kV and 300 mA with Cu Kα as a X-ray source. The step-scan patterns were collected in a range of 2° to 60° (2θ ranges) with a step size of 0.01° and a scan speed of 1° min^{-1}. The TEM and SEM images were taken with a HD-2300A (Hitachi) operated at 200 kV. Raman spectroscopy was performed using LabRAM HR UV–vis/NIR (Horiba Jobin Yvon) with a laser source of 514 nm. The XPS analysis was performed using a Sigma Probe (Thermo VG Scientific) equipped with a microfocused Al monochromator X-ray source. XPS-N_{1s} peaks were deconvoluted by pyridinic-N (398.6 eV), graphitic- or pyrrolic-N (401 ± 0.5 eV), and pyridinic-oxide (403 eV). The compositions of the prepared catalysts were obtained from an EA using a FlashEA 1112 and from an ICP analysis using a POLY SCAN 61 E.

2.3. Electrochemical characterizations

The electrochemical properties were characterized using a CHI700D (CH Instruments Inc.) and a RRDE-3A (ALS Co.) in a three-electrode beaker cell equipped with a Pt wire counter electrode (ALS Co., 002233), an Ag/AgCl reference electrode (ALS Co., 012167), and a ring disk electrode (ALS Co., 011169). The catalysts (10 mg) were dispersed in a Nafion ink solution (1 mL, 1 wt.% Nafion content), and then ink (5 μL) was dropped onto the glassy carbon (3 mm) of the ring disk electrode. The inks were dried at room temperature. Loading amount of the catalysts was 714 μg/cm^2. Cyclic voltammetry (CV) was conducted in a 1 M $HClO_4$ electrolyte purged with nitrogen or oxygen for more than 1 h, with a 40 mV/s scan rate from −0.22 to 1 V (vs. Ag/AgCl). The specific capacitance was obtained from the CV result in nitrogen-purged 1 M $HClO_4$ electrolyte by using the following equation:

$$C = \frac{\int I dt}{m \Delta V} \tag{1}$$

where C is the specific capacitance, I is the current from CV result, t is the time, m is the mass of the carbon material, and ΔV is the potential range.

Linear sweep voltammetry (LSV) was performed in a 1 M $HClO_4$ electrolyte purged by nitrogen or oxygen with a 5 mV/s scan rate from 0.82 to −0.08 V (vs. Ag/AgCl) and 2000 rpm rotation speed. The ORR currents were obtained by subtracting the LSV results for the nitrogen-purged electrolyte from those of the oxygen-purged electrolyte, in order to remove the capacitance of the catalysts. A Tafel-plot based on kinetic current in ORRs and ORR pathway was obtained by using Koutecky-Levich's equation:

$$\frac{1}{I} = \frac{1}{I_k} + \frac{1}{I_d} + \frac{1}{I_k} + \frac{1}{0.62 nFDA_{0_2}^{2/3} v^{-1/6} C_{0_2} \omega^{1/2}} \tag{2}$$